Available online at www.elixirpublishers.com (Elixir International Journal)

Crystal Growth

Elixir Crystal Growth 66 (2014) 20929-20931

ISSN: 2229-712X

Growth and characterization of high quality doped nonlinear optical crystals of L-Alanine Magnesium Chloride (LAMC)

P.Gandhimathi[1,*] and J Shanthi[2]

[1]Department of Physics, Kings Engineering College, Chennai, Tamilnadu.

[2]Department of Physics, Avinashilingam University for Women, Coimbatore-43 Tamilnadu

ARTICLE INFO

Article history:

Received: 5 June 2013;

Received in revised form:

20 January 2014;

Accepted: 23 January 2014;

Keywords

Electro optical properties,

UV-vis-NIR spectroscopy,

FTIR Spectroscopy,

Second harmonic generation (SHG).

ABSTRACT

Amino acids exhibit excellent nonlinear optical and electro optical properties. L-alanine magnesium chloride belongs to the amino acid group and has been grown by the slow evaporation solution growth technique (SEST) at room temperature. The grown crystals have been characterized by UV-vis-NIR spectroscopy; powder X-ray diffraction and Fourier transform infrared (FTIR) Spectroscopy. Second harmonic generation (SHG) efficiency of the grown crystal has been measured by Kurtz perry powder technique. The SHG efficiency of LAMC is found to be 0.3 times that of potassium dihydrogen orthophosphate (KDP).

Introduction

In recent years, the need of nonlinear optical materials is much more than other materials because of their applications in Optoelectronics and Photonics [1, 2]. With rapid progress in crystal growth technology, crystals having attractive NLO properties are being discovered. Organic materials are attractive due to their nonlinearities, ultra fast response time and relative ease of device processing. Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their non-linear optical (NLO) properties [3–6].Nonlinear optical crystal capable of generating second harmonic frequency plays an important role in the domain of optoelectronics and photonics. NLO crystals with high frequency conversion second harmonic efficiencies and transparent in the visible and ultraviolet ranges are required for numerous device applications. Most of the organic NLO crystals are constituted by weak Vander walls and hydrogen bonds with conjugated π electrons [7].In these respect amino acids are interesting materials for NLO applications [8].

Organic crystals are having some special properties of large optical nonlinearity and low cutoff wavelength in UV-region; therefore the organic NLO crystals are used in optical devices. However, the organic crystals have certain limitations such as poor mechanical and thermal stability. To overcome these problems, the combination of organic and inorganic hybrid compounds leads to find a new class of materials called semi organic materials having large optical nonlinearity, higher mechanical strength and chemical stability.

A survey of literature shows some complexes of L-alanine with inorganic salts such as LA acetate, LA cadmiumchloride, LA sodiumnitrate, Thiourea L-alanine acetate were reported(9-11). In this paper, we report the growth of L-alanine magnesium chloride (LAMC) by SEST. The title compound was characterized by various techniques.

Experimental:

Commercially available AR grades L-alanine and magnesium chloride were taken in the ratio 1:1 to synthesize LAMC. The calculated amount of reactants were thoroughly dissolved into double distilled water and stirred well for about 2h using a magnetic stirrer to obtain a homogeneous mixer. The solution was filtered using Whatmann filter paper to remove the suspended impurities. The filtered solution was taken in a beaker and covered by a perforated sheet. The solution was left undisturbed for evaporation at room temperature. After a span of period of 36 days, LAMC crystal of dimension (13mm×6mm×2mm) was harvested. The grown crystal is shown in figure 1.

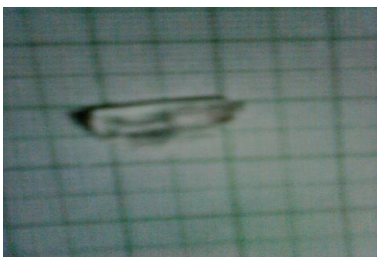

Figure 1. As grown crystal of lamc

Characterization:

UV-Visible spectral analysis:

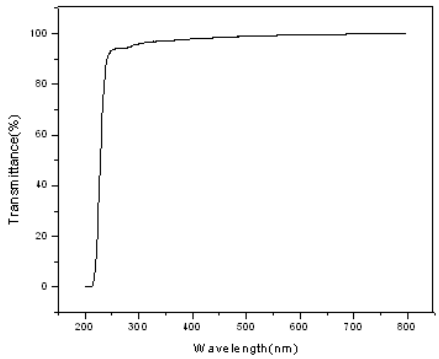

Figure 2. UV–Vis spectrum of LAMC single crystal

A good optical transmittance is desirable in an NLO crystal. Since the absorptions near the fundamental or the second

Tele:

E-mail addresses: nilageetham@rediffmail.com

harmonic of a Nd: YAG laser, will lead to a loss of SHG efficiency, and this has been a specific drawback in many organic crystal. As a matter of fact, many organic NLO materials with high nonlinear coefficients are often coloured and allow considerable absorption in the visible/near-UV region. Since the material requirement is for crystals capable of generating blue light by SHG from diode lasers, the desired lower cutoff in the transmittance analysis is to be between 200 and 400 nm [12].

The UV-vis-NIR transmittance spectrum is shown in figure 2. It was recorded with SHIMADZU UV-2501 IC, UV-Vis spectrometer in the range 190-800 nm. The crystal shows a good transmittance in the visible region. It is observed that there is no significant absorption in the range 190-800nm. As there is no absorption, the crystal is found to be transparent in the visible and near IR region, an essential parameter required for frequency doubling process [13]. This is advantage of the use of amino acids where the absence of strongly conjugated bonds leads to wider transparency ranges in the visible and UV spectral regions [14]. The lower cutoff at 210nm combined with the very good transparency window makes the material suitable for optoelectronics applications, the generation of the second and third harmonics of the Nd: YAG.

Powder X-ray diffraction studies:

The fine power of the title compound has been subjected to powder X-ray diffraction analysis and the recorded pattern is shown in figure [1]. The powder sample was scanned in steps of 0.1° for a time interval of 10 seconds over a 2Θ range of 10° to 70°. The sharp and well defined Bragg's peaks at specified 2Θ angles show the crystalline nature and purity of the crystal. New peaks in the XRD pattern of the grown crystal confirm the incorporation of magnesium chloride in the grown crystals.

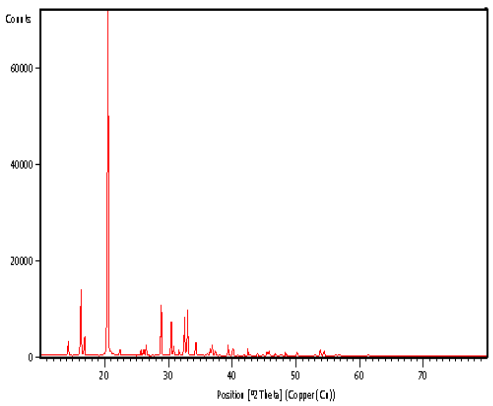

Figure 3. Powder X-ray diffraction pattern for LAMC

Single crystal XRD

The single crystal of LAMC has been subjected to single crystal XRD using The lattice paramaters determined for LAMC are a= 5.775A˚, b= 6.041A˚, and c= 12.335A˚, & α=β=γ=90° and the cell volume =431A˚. The structure is confirmed to be orthorhombic with the space group $P2_12_12_1$.

Fourier Transform Infrared (FTIR) analysis:

The infrared spectrum of the grown crystal has been taken using in the range of 400-4000cm^{-1}. The Fourier transform infrared (FTIR) spectrum of LAMC is shown in figure 4.The presence of the functional groups in LAMC crystal are identified. The peaks and their assignments are listed in table 1.

Amino group of absorption bands was noted at 844.82cm^{-1}. The peak at 2252.86 cm^{-1} is due to CH_3 stretching. The sharp absorption peak at 2110cm^{-1} is due to combination of NH^{3+} symmetric stretching and torsional oscillation. The peak at 1419.61cm^{-1} is due to symmetric stretching of C-COO$^-$.The peaks at 1149.57cm^{-1} and 1234.44cm^{-1} is due to NH_3^+ rocking. The peak at 412.27cm^{-1} is due to coo$^-$ rocking.

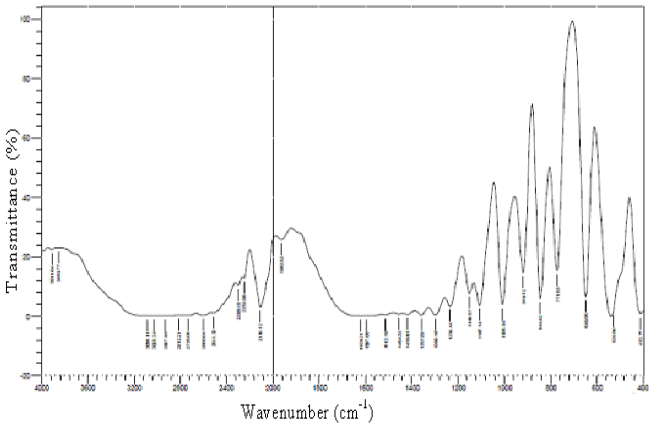

Figure 4. FTIR spectrum of LAMC

The C-C-N symmetric stretching vibration is confirmed by the presence of peak at 918.12cm^{-1}. The peak at 1107.14 cm^{-1} is due C-N stretching. The peak at 1006.84cm^{-1} represents C-N stretching. Due to C-CH_3 bending, a strong absorption peak was formed 844.82cm^{-1}.The peak at 771.53cm^{-1} is due to NO_3 stretching. The peak at 648.08 is due to COO^{-1} plane deformation. The peak at 528.5cm^{-1} represents torsional oscillation of NH_3^+.

Second Harmonic Generation:

The second harmonic generation (SHG) efficiency was determined by the modified version of the powder technique developed by Kurtz and Perry [15] using an Nd: YAG, 10 ns laser with a pulse repetition rate of 10Hz working at 1064 nm. The sample was ground into fine powder and tightly packed in a micro-capillary tube. It was mounted in the path of the laser beam of 3.6mJ pulse energy obtained by splitting the original laser beam. The output light was passed through a monochromator transmitting only the second harmonic (green) light at 532nm.The green light intensity was registered by a photomultiplier tube and converted into an electrical signal. This signal was displayed on the oscilloscope screen.

Potassium dihydrogen orthophosphate (KDP) ground into samples of identical size was used as reference material in the SHG measurements conversion efficiency was computed by the ratio of amplitude of the LAMC and LACC sample to that of the KDP signal amplitude recorded for the same input powder. The SHG efficiency of the grown LAMC crystal was found to be 0.3 times higher than that of KDP.

The efficiency of the frequency conversion will vary with the particle size and the orientation of the crystallites in the capillary tube. Hence, higher efficiency may be expected to be achieved with single crystals by optimizing the phase matching (16).

Conclusion

LAMC crystal has been grown from aqueous solution by slow evaporation technique at room temperature. The sharp and well defined Bragg's peaks of powder XRD pattern at specified 2Θ angles shows the crystalline nature and purity of the crystal. The lattice parameters of LAMC are determined by single crystal XRD. It belongs to orthorhombic crystal system with the space group $P2_12_12_1$.The FTIR analyses confirm the presence of various functional groups. The lower cutoff wavelength at 210nm and the wide transparency range (190nm–800nm) observed from the UV–Vis spectrum confirms its suitability of the material for SHG applications. SHG studies revealed that LAMC crystals are a promising material for NLO applications.

References

[1] D.S Chemla and J.Zyss (Eds) Nonlinear Optical properties of organic molecule and crystal, Vol 1& 2, Academic Press, New York.
[2]R.W. Boyd, Nonlinear Optics, Academic Press, San Diego (1992).
[3] M. Kitazawa, R. Higuchi, M. Takahashi, Appl. Phys. Lett.64 (1994) 2477.
[4] L. Misoguti, A.T. Varela, F.D. Nunes, V.S. Bagnato,F.E.A. Melo, J. Mendes Filho, S.C. Zilio, Opt. Mater. 6(1996) 147.
[5] W.S. Wang, M.D. Aggarwal, J. Choi, T. Gebre, A.D.Shields, B.G. Penn, D.O. Frazier, J. Crystal Growth 198/199 (1999) 578.
[6] S. Chenthamarai, D. Jayaraman, P.M. Ushasree, K.Meera, C. Subramanian, P. Ramasamy, Mater. Chem.Phys. 64 (2000) 179.
[7] D.Xu., M.Jang.,Z.Ton., Acta chem.sin.,41(1983)570.
[8] Tapati Mallik.,Tanusree Kar.,Journal of crystal Growth, 285(2005) 178.
[9] K.C.Bright, T.H.Freeda, Physica B,405(2010)3857-3861.
[10] Neelamsingh, B.K.Singh, NidhiSinha, Binaykumar. Journal of crystal Growth,310(2008)4487-4492.
[11] K.Sethuraman, R.Ramesh Babu, R.Gopalakrishnan, P.Ramasamy, Crystal Growth and design(2008)1863-1869.
[12] Y. Le Fur,R. Masse, M.Z.Cherkaoui, J.F.Nicoud, Z.Kristallogr. 210 (1995)856.
[13] C.N.R.Rao, Ultraviolet and visible Spectroscopy of organic compound, Prentice Hall Pvt. Ltd., New Delhi 1984 , 60-64.
[14] C. Razzetti, M. Ardoino, L. Zanotti, M. Zha, C. Parorici, Cryst. Res. Technol. 37(2002) 456.
[15] S.K.Kurtz.,T.T.Perry,J.Appl.Phy, 39(1968)3798-3813.
[16] M.Narayan Bhat, S.Dharmaprakash J. Crystal Growth 236 2003) 376.